Physico-chemical Treatability of Olive Mill Wastewater (OMW)

Abstract: In this study, physico-chemical treatability of olive mill wastewater (OMW) arises from a plant which produces olive oil according to three-phase system in Edremit-Balıkesir has been investigated. First of all, it has been separated fatty parts from OMW due to having high BOD, COD, MLSS, oil&grease, and continuous methods (two-phase and three-phase) in centrifugation method (three-phase and two-phase) in continuous press method or the continuous distillation (Oktav and De Rosa et al., 2005; Sarika et al., 2005; Ginos et al., 2006), chemical+biological treatment (Bressan et al., 2004), land disposal (Kocaer et al., 2004), electrocoagulation (Inan et al., 2001; Oktav et al., 2003; Girigeropoulos, 1993; Scioli and Vollaro, 1997), phenol values in the range of 0.5-24 g/L (Paraskeva and Girigeropoulos, 1993; Cossu et al., 1993; Azzam et al., 2000), COD values in the range of 80-200 g/L (Boari and Mancini, 1990; Tsonis and Girigeropoulos, 1993; Scioli and Vollaro, 1997), phenol values in the range of 0.5-24 g/L (Paraskeva and Diamadopoulos, 2006).

Treatment of OMW is difficult and treatment cost is very high because of having high organic pollution and long-chain fatty acids and phenolic compounds which are hard to biodegrade of OMW, scattering high territorial of small olive oil producers, doing the production of olive oil in three or four months.

It has necessary combination of many treatment methods for treatability of OMW. In treatability studies of OMW in literature have been used a lot of methods such as aerobic treatment (Fadil et al., 2003; Tziotzios et al., 2007), anaerobic treatment (Ergüder et al., 2000), aerobic treatment + fenton oxidation (Kotsou et al., 2004), chemical treatment (Aktaş et al., 2001; Oktav et al., 2003; De Rosa et al., 2005; Sarika et al., 2005; Ginos et al., 2006), distillation (Oktav and Şengül, 2003), chemical+biological treatment (Bressan et al., 2004), land disposal (Kocaer et al., 2004), electrocoagulation (Inan et

Introduction

Olive and olive oil production which have important position in agricultural activities, have intensified in the Mediterranean Region and become widespread in the world. It is estimated that the annual world production of olive oil and table olives (black and green) is about 2.5, 10⁶ and 10⁶ tons, respectively, with Spain, Italy and Greece being the major producers (Brenes et al., 1999). There has been a recent rise though in other countries as well, such as Canada, Australia, Japan and the US. Other important olive-producing countries are Turkey, Tunisia, Morocco, Syria, Portugal, United States, Canada, Australia and Japan (Arvanitoyannis et al., 2007).

Olive oil is produced from olives either by the discontinuous press method or the continuous centrifugation method (three-phase and two-phase) in nowadays. Two by-products such as bagasse and olive mill wastewater (OMW) are obtained from olive oil in these two methods. It is produced 0.4-0.5 m³ and 1-1.5 m³ wastewater, respectively for 1 ton olive in discontinuous and continuous methods (Şengül et al., 2002).

OMW has essentially contain materials which are in olive. This wastewater has an important pollute potential due to having high BOD, COD, MLSS, oil&grease, phenol and polyphenol compounds which are phytotoxic (Hamdi, 1993; Kavakhl, 2002). OMW has BOD values in the range of 12-63 g/L (Cossu et al., 1993; Azzam et al., 2004; Al-Malah et al., 2000), COD values in the range of 80-200 g/L (Boari and Mancini, 1990; Tsonis and Girigeropoulos, 1993; Scioli and Vollaro, 1997), phenol values in the range of 0.5-24 g/L (Paraskeva and Diamadopoulos, 2006).
al., 2004; Tezcan Ün et al., 2006), adsorption (Al Malah et al., 2000; Azzam et al., 2004), advanced oxidation processes (Canizares et al., 2007), membrane processes (Paraskeva et al., 2007), electrofenton (Khoufi et al., 2004), electrofenton+anaerobic treatment (Khoufi et al., 2006), composting (Vlyssides et al., 1996).

Many studies have been done for treatment of OMW in Turkey and in the world. Oktav et al., (2003) obtained 13% COD removal efficiency by using lime and 38% by using HCl in chemical precipitation. They used KMnO₄, NaOCl, H₂O₂ and Fenton’s Reagent in chemical oxidation study and obtained 70% COD removal efficiency. Physico-chemical treatment and advanced oxidation processes (H₂O₂/UV and O₃/UV) were carried out by Kestioğlu et al., (2005). They obtained 38% COD and 23% total phenol removal efficiency in acid cracking, 94% COD and 91% total phenol removal efficiency in acid cracking+alum coagulation, 95% COD and 90% total phenol removal efficiency in acid cracking+FeCl₃ coagulation, 99% COD and total phenol removal efficiency in the whole processes. Ginos et al., (2006) investigated the pre-treatment of OMW by means of coagulation-flocculation coupling various inorganic materials and organic polyelectrolytes and obtained COD and TP removal varied between about 10-40% and 30-80%, respectively. To enhance organic matter degradation, iron-based coagulation was coupled with H₂O₂ and this increased COD reduction to about 60%. In this study, OMW from a plant which produces olive oil according to three-phase system in Edremit-Balikesir has been investigated. Acid cracking and chemical treatment have been carried out in OMW which characterized and the results of physico-chemical treatability have been explained as COD removal efficiency.

**Materials and Methods**

In this study the analysis of OMW were done according to Standard Methods (APHA, AWWA, WCPF, 1998). The jar test apparatus was a Velp Scientifica apparatus with six stirrers. MLSS mechanism and pH meter were from Sartorius. Chitosan was solubilized in 50% acetic acid solutions and mixed at a temperature of 50 ºC (Meyssami and Kasaeian, 2005).

For breaking oils, first of all acid cracking were applied to OMW. pH were dropped to 1.3 adding 7 ml 96% H₂SO₄ to 1 L wastewater in acid cracking. The oily parts were peeled off sample and COD, MLSS and phenol were analysed at supernatant.

The Jar Tests were done in wastewater from acid cracking adding FeCl₃ (500-2500 mg/L), Chitosan (30-70 mg/L) and SDS (0.2-1 g/L). The pH were increased to 6 with 25% NaOH as study done by Meyssami and Kasaeian, (2005), then amount of two coagulants were constant and amount of other coagulant were changed. After stirring times between 5 and 30 min and stirring speeds between 15 and 90 rpm, the samples were settled 1 hour and COD were analysed at supernatant.

**Results and Discussion**

The characteristics of OMW used in this study are given in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>4.95</td>
</tr>
<tr>
<td>Electric conductivity</td>
<td>mS/cm</td>
<td>7.00</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>128000</td>
</tr>
<tr>
<td>MLSS</td>
<td>mg/L</td>
<td>27000</td>
</tr>
<tr>
<td>Oil&amp;grease</td>
<td>mg/L</td>
<td>10000</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/L</td>
<td>3760</td>
</tr>
</tbody>
</table>

**Acid Cracking**

COD, MLSS and phenol removal efficiencies after acid cracking were given in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Entry Value</th>
<th>Exit Value</th>
<th>Removal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>4.95</td>
<td>1.3</td>
<td>53</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>128000</td>
<td>60000</td>
<td>53</td>
</tr>
<tr>
<td>MLSS</td>
<td>mg/L</td>
<td>27000</td>
<td>2500</td>
<td>91</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/L</td>
<td>3760</td>
<td>2580</td>
<td>31</td>
</tr>
</tbody>
</table>

**Chemical Treatability Study**

The aim of the coagulation step was to remove COD from OMW using Chitosan, SDS and FeCl₃ together. Accordingly the coagulation efficiency was investigated in terms of COD removal.

It was added 50 mg/L Chitosan, 0.6 g/L SDS and 500, 1000, 1500, 2000, 2500 mg /L FeCl₃ to vessels for determination of optimum FeCl₃ dosages at pH=6 in OMW after acid cracking. Exit COD values in different FeCl₃ dosages were shown in Figure 1. The optimum coagulant dosage of FeCl₃ was determined as 2500 mg/L as seen in Figure 1.
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**Figure 1.** Exit COD Values in Different FeCl₃ Dosages (pH=6; Chitosan=50 mg/L, SDS=0.6 g/L)

For determination of optimum Chitosan dosages in Jar Tests after acid cracking, it was added 0.6 g/L SDS, 2500 mg/L FeCl₃ and 30, 40, 50, 60, 70 mg/L Chitosan to OMW (pH=6) in vessels and exit COD values in different Chitosan dosages were shown in Figure 2.

**Figure 2.** Exit COD Values in Different Chitosan Dosages (pH=6; SDS=0.6 g/L; FeCl₃=2500 mg/L)

In OMW (pH=6) 50 mg/L Chitosan, 2500 mg/L FeCl₃ and 0.2; 0.4; 0.6; 0.8; 1 g/L SDS was added to vessels after acid cracking for determination of optimum SDS dosages. Exit COD values in different SDS dosages after Jar Test were shown in Figure 3.

**Figure 3.** Exit COD Values in Different SDS Dosages (pH=6; Chitosan=50 mg/L; FeCl₃=2500 mg/L)
The COD values after optimum dosages of Chitosan (50 mg/L) and SDS (0.6 g/L) were increased as seen in Figure 2 and 3, because of interference between potassium dichromate and coagulants in COD test.

As a result of chemical treatment, optimum coagulant dosages of Chitosan, SDS and FeCl$_3$ was determined as 50 mg/L, 0.6 g/L, 2500 mg/L, respectively. COD, MLSS and phenol removal efficiencies in these dosages were obtained as 68%, 28% and 25%, respectively and 100 ml/L sludge was obtained at the end of this process. The removal efficiencies determined in this study, are similar to some studies done by Meyssami and Kasaeian (2005), Rizzo et al., (2008) and Ginos et al., (2006).

Meyssami and Kasaeian, (2005) investigated the use of chitosan in the treatment of olive oil wastewater model solutions. In the jar experiments, they used chitosan and alum together at concentrations of 15 and 25 ppm, respectively, at pH 6 and obtained the lowest turbidity values in these conditions. Rizzo et al., (2008) studied coagulation with chitosan and advanced oxidation processes on OMW. They achieved 81% TSS removal at pH 4.3 for 400 mg/L chitosan dosage. Ginos et al., (2006) investigated the OMW treatment by the combined use of coagulants (Fe(III), ferrous sulphate (FS), magnesium sulphate (MS) and PACl), the two OMW samples (W1 and W2) being characterized by higher TSS concentrations (36.7 and 52.7 mg/L) and pH values (5.3 and 5.3) and comparable COD concentrations (61.1 and 29.3 g/L) with respect to OMW sample investigated in the present work. The best TSS removal they detected were 14, 60, 90 and 95% with 1000 mg/L of FC, PACl, MS and FS, respectively.

The cost of chemical materials used in this physico-chemical treatability study was calculated according to market prices. Total daily chemical material cost was determined as 6807.83 Euro for a flow of 100 m$^3$/day (Table 3).

### Table 3. The cost of daily chemical material used in treatment plant

<table>
<thead>
<tr>
<th>Chemical Material</th>
<th>Required dosage</th>
<th>Daily used dosage</th>
<th>Unit Price</th>
<th>Total Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technics sulphuric acid</td>
<td>7 ml/L</td>
<td>700 L/d</td>
<td>1.4 Euro/L</td>
<td>980 Euro/d</td>
</tr>
<tr>
<td>Chitosan</td>
<td>50 mg/L</td>
<td>5 kg/d</td>
<td>500 Euro/kg</td>
<td>2500 Euro/d</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>2500 mg/L</td>
<td>250 kg/d</td>
<td>2.27 Euro/kg</td>
<td>567.5 Euro/d</td>
</tr>
<tr>
<td>SDS</td>
<td>0.6 g/L</td>
<td>60 kg/d</td>
<td>20.7 Euro/kg</td>
<td>1242 Euro/d</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>2.5 L/d</td>
<td>2.5 L/d</td>
<td>3.3 Euro/L</td>
<td>8.25 Euro/d</td>
</tr>
<tr>
<td>NaOH</td>
<td>57.2 ml/L</td>
<td>1716 kg/d</td>
<td>0.88 Euro/kg</td>
<td>1510.08 Euro/d</td>
</tr>
<tr>
<td><strong>Total cost</strong></td>
<td></td>
<td></td>
<td><strong>6807.83 Euro/d</strong></td>
<td></td>
</tr>
</tbody>
</table>

### Conclusion

In this study, physico-chemical treatability of OMW arises from a plant which produces olive oil according to three-phase system in Edremit-Balıkesir has been investigated. The oil-grease was removed by acid craking before chemical treatment using Chitosan, SDS (Sodium Dodecly Sulfate) and FeCl$_3$. The optimum dosages of Chitosan, SDS and FeCl$_3$ at pH=6 were found as 50 mg/L, 0.6 mg/L and 2500 mg/L, respectively.

As a result of this study, COD, MLSS and phenol were decreased to 19200 mg/L, 1800 mg/L and 1940 mg/L, respectively with a 85% COD, 93% MLSS and 48% phenol removal efficiencies by the combination of acid cracking and chemical treatment in the optimum conditions. The COD was largely removed by physico-chemical treatment, but it wasn’t reached to discharge standard given in Table 5.5 in Turkish Water Pollution Control Regulation (Anonymous, 2004). It has required a combination of physico-chemical and advanced treatment methods reaching discharge standards for receive environment. Also, the chemical material cost has been calculated as 6807.83 Euro for a factory with a flow of 100 m$^3$/day. At the end of this study, it has been considered that the physico-chemical treatability with these coagulants of OMW isn’t economic. So that, it has been thought that treatability studies with different processes should apply.

### Acknowledgement

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### References


